

Chapter 3



Rocky Mountain National Park, CO (ROM206/406)

DQI Measurement Results

Precision

As discussed in Chapter 2, when evaluating the precision of atmospheric concentrations, two particular factors must be considered. The first is the tendency toward higher variability (i.e., more “noise”) as readings approach limits of detection. The other is that the historical precision of the particulate NO_3^- measurements has been consistently worse than for the other analytes, possibly because 1) nitrate concentrations are the lowest of all the pollutants, and 2) nitrate species are in a dynamic equilibrium on and between filters involving gas and particle phases. This equilibrium is affected by changes in air temperature and humidity.

The tendency toward greater variability in measurements of lower concentrations has been addressed in the laboratory precision criteria listed in the latest revision of the CASTNet QAPP (MACTEC, 2003b) via establishment of a “sliding” window that allows for greater imprecision as concentrations approach reporting limits.

The low levels of nitrate concentrations are also impacted by the dynamic nature of nitrate gas and particle phases since the dynamic equilibrium of nitrate concentrations directly affects the measurements obtained from the filter media. For example, the ammonium nitrate aerosol collected on the Teflon[®] filter may volatilize and form gaseous HNO_3 , which in turn could migrate to the nylon filter, thereby changing concentrations of NO_3^- , NH_4^+ , and HNO_3 .

The dissociation of ammonium nitrate collected on the Teflon[®] filter tends to result in overestimation of HNO_3 concentrations and underestimation of NO_3^- and NH_4^+ concentrations. The available information suggests that modeled dry nitrogen deposition is overestimated by 10 to 20 percent as a result of these biases while the uncertainty in total nitrogen deposition is less than a 10 percent overestimate. Please see Chapter 3 of the CASTNet 2002 Annual

Report (MACTEC, 2003a) for a more detailed discussion of uncertainties in estimation of nitrogen deposition.

Field Collocated Sampling Systems

During 2002, collocated sampling systems were operated at Mackville, KY (MCK131/231) and Rocky Mountain National Park, CO (ROM206/406). The systems in Kentucky are both operated by EPA with common site operators and calibrators. The site at Rocky Mountain National Park, CO has two independent systems. EPA operates ROM206 while NPS operates ROM406. The Colorado sites are operated by different site operators and calibrated by different calibrators. The two sets of collocated sampling systems offer an opportunity to compare intra-system and inter-system measurements.

In Figure 4, the bars on the chart present precision statistics for concentration measurements of sulfur and nitrogen species in terms of MARPD for both the historical database (i.e., 1990 through 2001) and the 2002 data for MCK131/231 and ROM206/406. Historically, collocated systems have been operated at 11 sites. The historical results vary from about 5 percent for particulate SO_4^{2-} to about 12 percent for particulate NO_3^- . The historical MARPD statistics for SO_4^{2-} and NH_4^+ meet the criteria in Table 2. The results for SO_2 and HNO_3 are above the 5 percent criterion but are considered reasonable. The results for NO_3^- are significantly above the 5 percent goal.

As mentioned previously, historically, the precision of the particulate NO_3^- measurements has been consistently worse than for the other analytes. In other words, NO_3^- and NH_4^+ concentrations could be underestimated and HNO_3 overestimated. This dynamic equilibrium combined with the low concentrations measured possibly leads to the continued high MARPD for both the historical and 2002 measurements.

Precision statistics for 2002 for trace cations are summarized in Figure 5. The precision criterion is 10 percent for both collocated ambient concentrations and laboratory in-run replicates. The laboratory in-run replicate results for all cations for all sites met the criterion. The MARPD data for the collocated measurements of potassium (K^+) and magnesium (Mg^{2+}) were acceptable for both sets of sites. The precision data for collocated calcium (Ca^{2+}) concentrations were acceptable for MCK131/231 but exceeded the criterion at ROM206/406. The precision statistics for collocated Na^+ measurements were well above the 10 percent goal for both sites.

Table 7 summarizes precision results by quarter for the two sets of collocated systems. An investigation of Na^+ data (described in detail in the 2001 QA Report) indicated that the source of contamination was the laboratory sample bottles purchased from a certain manufacturer between 1999 and 2001 (Harding ESE, 2003). The bottles showing contamination were used between

March 1999 and March 2002. As noted in the 2001 QA Report, bottles are no longer purchased from this manufacturer.

MACTEC recommends that Na^+ data for Teflon[®] filters extracted between March 1999 and March 2002 be invalidated.

As part of the additional QA/QC procedures instituted in response to the bottle

investigation, the filter media acceptance testing program now includes the four cations, Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . The acceptance testing program for filter media previously only performed tests for anion and NH_4^+ parameters. If test results exceed the reporting limits for any of the parameters shown in Table 2, the associated box of filters is rejected.

Figure 4. Historical and 2002 Precision Data for Sulfur and Nitrogen Species

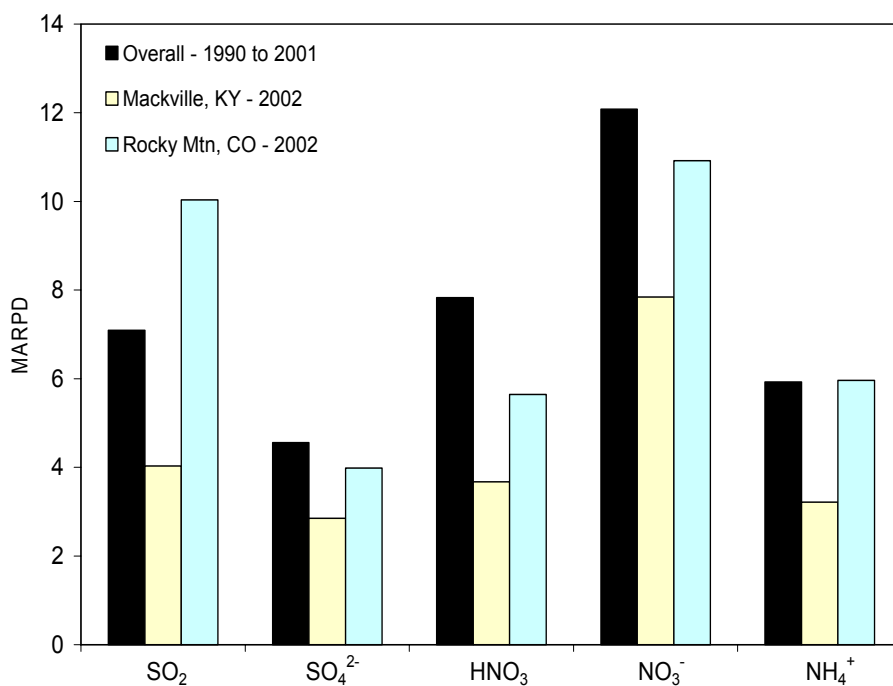
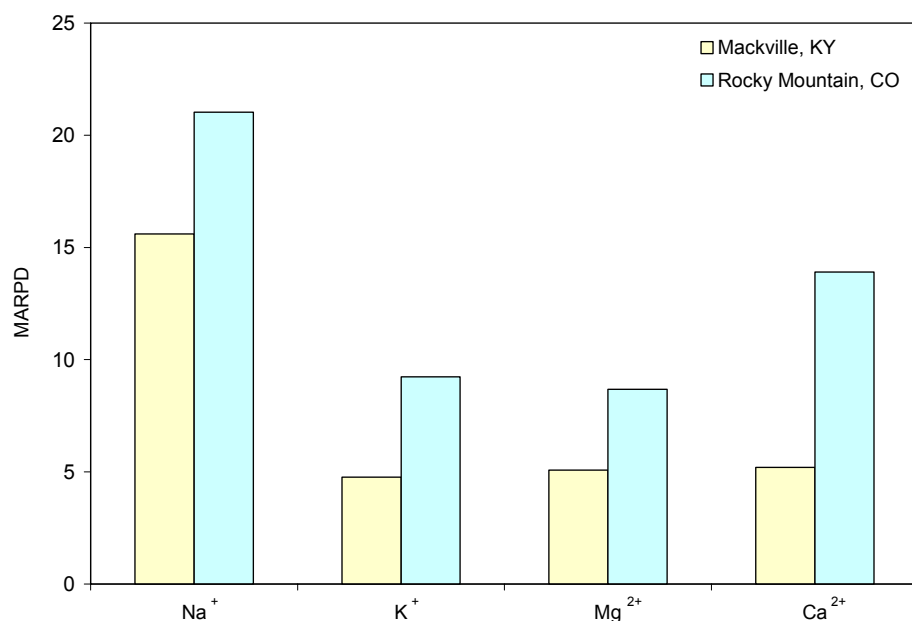


Figure 5. Precision Data for Cation Concentrations for 2002**Table 7.** Precision Results by Quarter for 2002

Site Pairs	SO ₂	NO ₃	NH ₄	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HNO ₃	SO ₂	Total NO ₃
MCK 131/231										
Q1	5.27	3.83	5.33	5.15	5.98	41.79	4.00	4.21	6.14	3.75
Q2	1.34	10.86	1.32	4.76	4.81	2.30	3.68	3.68	3.31	3.49
Q3	2.32	9.16	3.35	5.75	4.51	2.81	6.44	3.59	2.98	3.73
Q4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2002	2.98	7.95	3.33	5.22	5.10	15.63	4.71	3.83	4.14	3.66
ROM 406/206										
Q1	2.54	9.99	5.01	4.95	4.94	57.86	8.39	4.48	7.97	2.44
Q2	4.18	6.87	4.71	4.21	5.46	9.74	8.00	7.16	10.13	4.21
Q3	5.25	9.66	7.08	17.46	7.60	6.38	5.91	4.10	11.35	4.26
Q4	3.42	14.05	5.55	25.84	12.29	8.21	12.69	4.94	11.86	5.69
2002	3.85	10.14	5.59	13.12	7.57	20.55	8.75	5.17	10.33	4.15

Note:

25 parameters outside criterion.

N/A Not available because of incomplete data.

Laboratory Analysis

The 2002 analytical precision results for five analytes and the three filter types are presented in Figure 6 using a scale of zero to 14 percent to match the scale of the collocated sample data presented in Figure 4. The results presented in Figure 6 are based on re-analysis of 5 percent of all samples. Samples were randomly selected for replication within each batch. The results of the analyses of the in-run replicates were compared to the results of original concentrations. The laboratory precision data met the 5 percent measurement criterion listed in Table 2.

The collocated precision data for continuous field measurements from 1990 through 2002 are presented in Figure 7. MARPD results were all less than 7 percent with flow rate,

ozone, and wind direction less than 5 percent. Solar radiation values below 5 watts per square meter (W/m^2) were not considered in the calculation. MAD results were all less than 0.14. All were well within the precision criteria given in Table 3 regardless of unit even when the accuracy criterion was substituted (relative humidity and scalar wind speed criteria are range dependent; however, both parameters still show MARPD less than 6 percent). For example, the precipitation accuracy requirement is 0.05 inch and the MAD is less than 0.02.

The MARPD is used for all parameters except temperature, delta temperature, precipitation, and wetness. The MAD is used for these parameters because the values are routinely too small to calculate a meaningful MARPD.

Figure 6. Laboratory Precision Data for 2002

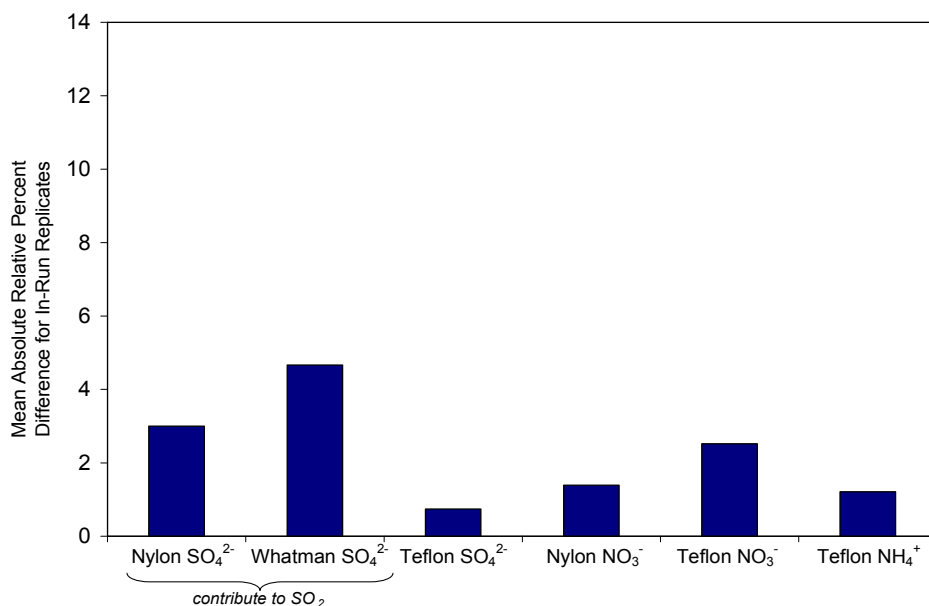
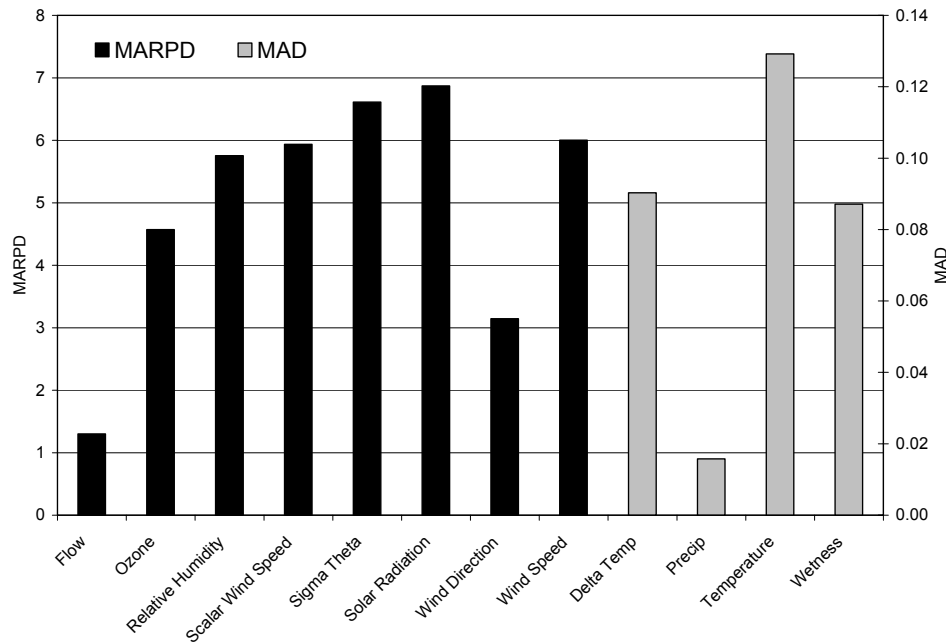


Figure 7. Precision Statistics for Continuous Parameters at CASTNet Collocated Site Pairs (1990-2002)



Accuracy

Field Collocated Sampling Systems

CASTNet sites are calibrated every six months with NIST-traceable standards. The results of the initial instrument challenges performed during each calibration during 2002 were used to compile the site accuracy results shown in Table 8. All parameters were within the criteria shown in Table 3 more than 90 percent of the time, except for relative humidity > 85 percent and solar radiation. These parameters met established criteria 81 percent and 88 percent of the time, respectively. According to CASTNet project protocols, associated data are still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). The percent

within 2x criterion for these parameters was 97 percent and 100 percent, respectively. Therefore, the completeness results for these parameters were not adversely affected.

The frequency of site calibration was reduced from a quarterly to a semiannual schedule beginning in 2000, and tighter measurement criteria limits were established for relative humidity > 85 percent and filter pack flow rate. The average percentage of sites meeting the criteria for these two parameters before 2000 was greater than 95 percent. The average percentage after 2000 is 85 percent for relative humidity > 85 percent and 91 percent for filter pack flow rate.

Historically, solar radiation has met the criterion at a lower frequency than any other parameter. The average percentage meeting the criterion before 2000 was 93 percent. The average percentage after 2000 is 90 percent.

Laboratory Analysis

Accuracy of laboratory measurements is assessed through the analysis of reference samples and calibration verification samples (CVS). Reference samples and CVS are procured from independent suppliers and are NIST traceable.

Reference samples are analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the

calibration curve. The criteria are five percent for anions and 10 percent for cations (Table 2). Figure 8 presents the percent recovery relative to each certified reference value and its standard deviation for 2002.

Accuracy is also assessed through the analysis of NIST-traceable CVS. The target value of the CVS solution is set to the midrange of the calibration curve. The CVS in 2002 were analyzed every tenth sample to verify that any drift in the calibration curve stayed within accuracy limits (Table 2).

Figure 9 presents the percent recovery of the CVS relative to the target concentrations.

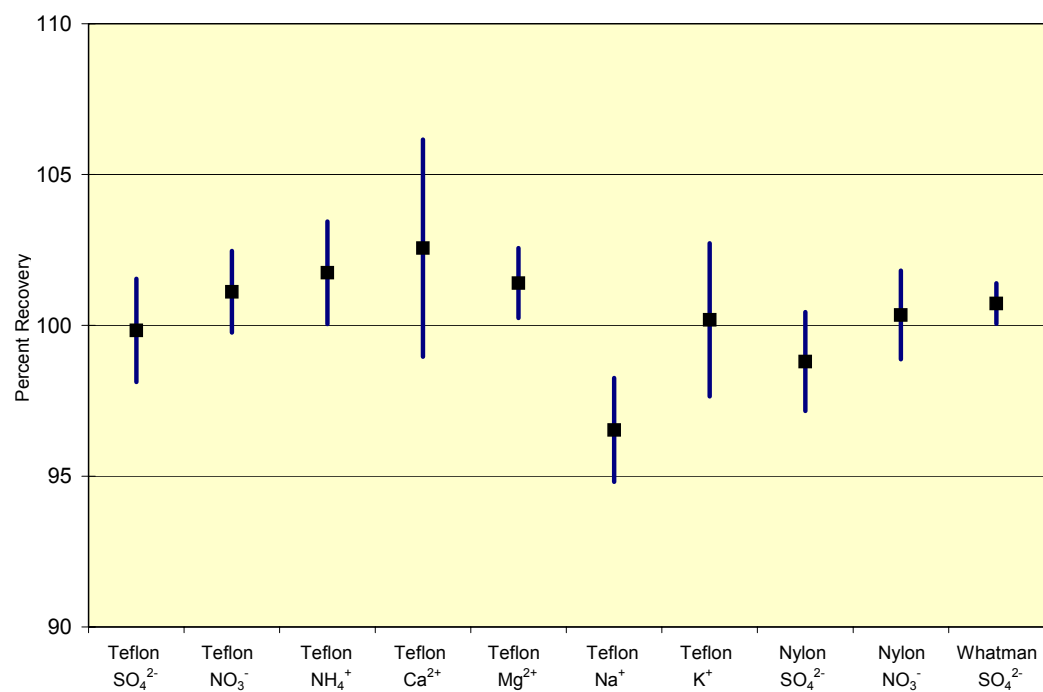
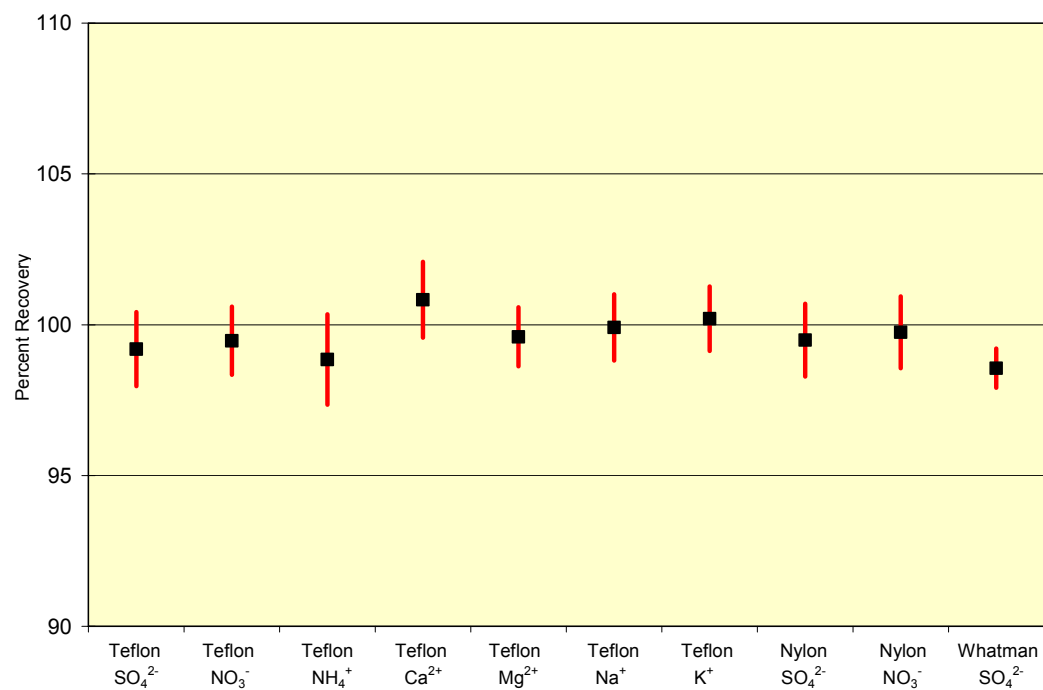
The standard deviation of each of the recovery values is also plotted. During 2002, the DQI goals for CVS accuracy were met for all analytes and all filter types.

Table 8. 2002 Accuracy Results for Continuous Field Measurements

Parameter	Percent Within Criterion
Temperature (0°C)	96 percent
Temperature (ambient)	96 percent
Delta Temperature (0°C)	97 percent
Delta Temperature (ambient)	98 percent
*Relative Humidity > 85%	81 percent
Relative Humidity ≤ 50%	99 percent
*Solar Radiation	88 percent
Wind Direction North	91 percent
Wind Direction South	94 percent
Wind Speed < 5 m/s	100 percent
Wind Speed ≥ 5 m/s	99 percent
Precipitation	99 percent
Wetness (w/in 0.5 volts)	98 percent
Ozone Slope	97 percent
Ozone Intercept	99 percent
Flow Rate	92 percent

Note:

- °C = degrees Celsius.
- m/s = meters per second.
- * = Per CASTNet project protocols, data are flagged as “suspect” (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). The percent within 2x criterion for these parameters was 97 percent and 100 percent, respectively.

Figure 8. Reference Sample Recovery for 2002**Figure 9.** Calibration Verification Samples for 2002**Note:**

The square represents the sample recovery and the spread around the square represents its standard deviation.

Bias

Bias may be defined as the systematic or persistent distortion of a measurement process that causes errors in one direction.

Field Collocated Sampling Systems

Bias in continuous data is assessed by monitoring internal performance evaluation audit results over time. The differences between audit/calibration standards and site instrumentation readings are calculated. Bias is assessed annually using data from specified parameters collected over a minimum of two years at selected sites.

Figure 10 shows the locations of Group 1 and Group 4 sites, which were used to assess bias. Figures 11a through 11d show these results for calibration Group 1 (January/July calibrations, several southern sites) and Group 4 (April/October calibrations, several northern sites). The NPS-sponsored sites, designated by the 400 series site numbers (format = abc4xy), are present on the map in Figure 10, but are not included in this field calibration analysis. Results are calculated as indicated in Table 3 with the exception of ozone, which is displayed as the actual value. As indicated in Table 8, CASTNet ozone monitors are quite stable and generally show only very small variation. Temperature, delta temperature, precipitation, and wetness parameters are presented separately because the values are significantly smaller than those for other parameters and require a different scale. Large spikes are generally due to one site skewing the data as depicted in Figures 11a

through 11d. Calibration failures at sites SAL133, IN and WST109, NH skewed the wind direction calibration data recorded for Group 4 sites from September to November 2001 and September to October 2002. When these particular calibrations are excluded from the analysis, there is no consistent bias seen in field calibrations. The affected data were flagged appropriately.

Laboratory Analysis

The assessment of analytical bias is accomplished through the monitoring of reference sample recoveries over time via graphics and charts. The range of acceptable bias is bounded by the accuracy criterion for the parameter and method. CASTNet criteria are 5 percent for sulfate and nitrate and 10 percent for ammonium and cations (Table 2). Figure 12 presents the percent recovery relative to the certified reference values for 2002. All analytes representing all filter types met the criteria.

The graphics and charts used to track bias also reveal the changes in reference sample lots, instrumentation, and procedures. For instance, changes in the reference response pattern for sulfate and nitrate measurements are depicted on the charts in Figure 12 starting in late April. These changes correlate with a new ion chromatography instrument coming on line. Please note that the same SOP, columns, and separation technology were used with the new instrument as had been used with the previous instrument. Similarly, the reference

response pattern for nitrate changed in July, which reflects a change to calibration standards having preserved separately the nitrate/nitrite fractions.

Figure 13 presents the percent recoveries for CVS analyzed during 2002 relative to their certified values. The response pattern depicted is similar to that for the reference samples (Figure 12). Pattern variation is discernable in late April and again in July due to the same instrument and calibration standard changes noted for the reference

sample response. All analytes representing all filter types met criteria with the exception of a single CVS analyzed on 5/9/2002. The recovery for this CVS was 93 percent for both sulfate and nitrate on the Teflon[®] filter. The laboratory analyst, upon examination of the chromatogram, noted that the low recovery was due to a single “bad injection” as determined by the internal standard peak area. All samples analyzed before and after this CVS were field blanks with no measured response above the detection limit. The data for these samples should be acceptable.

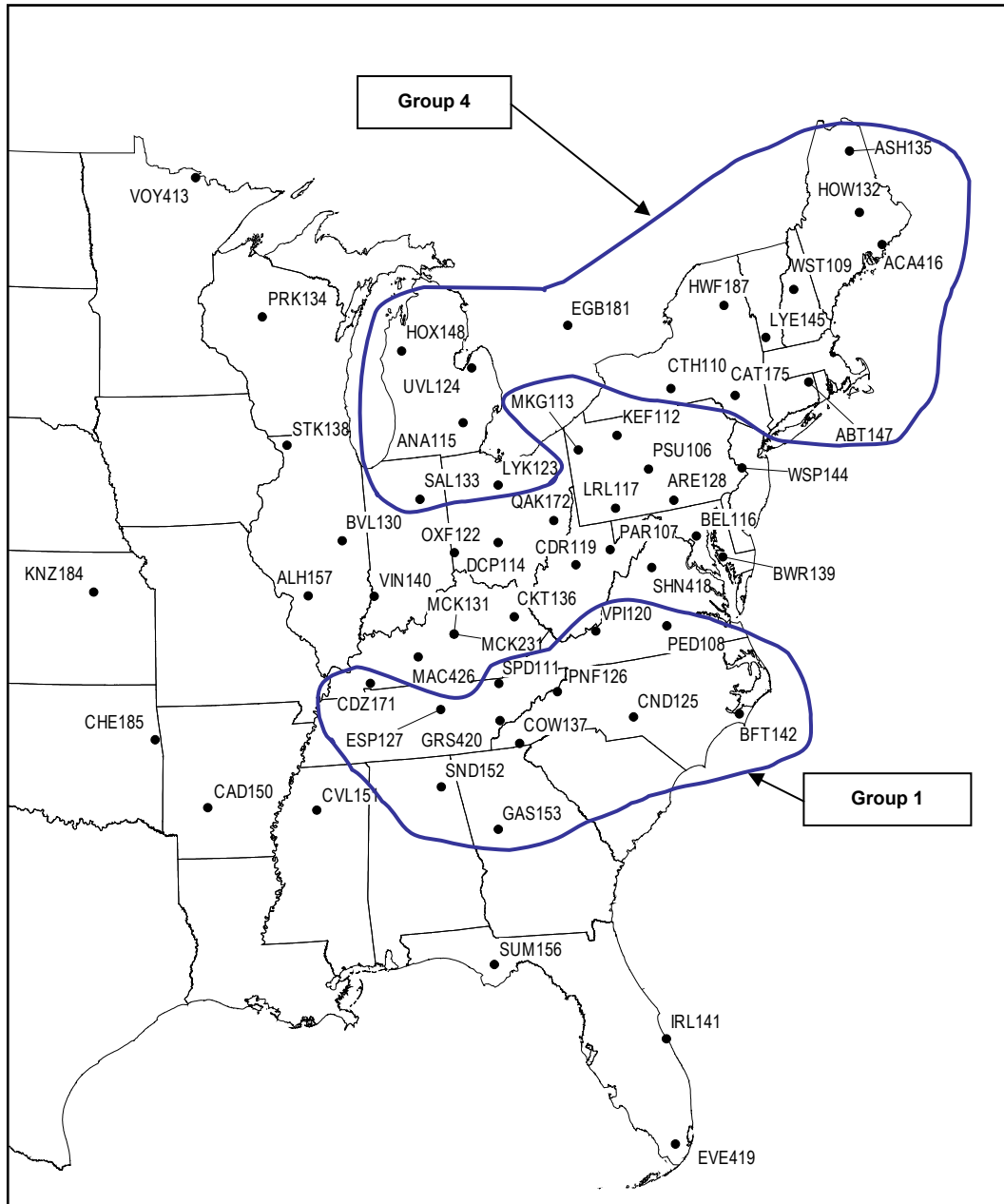
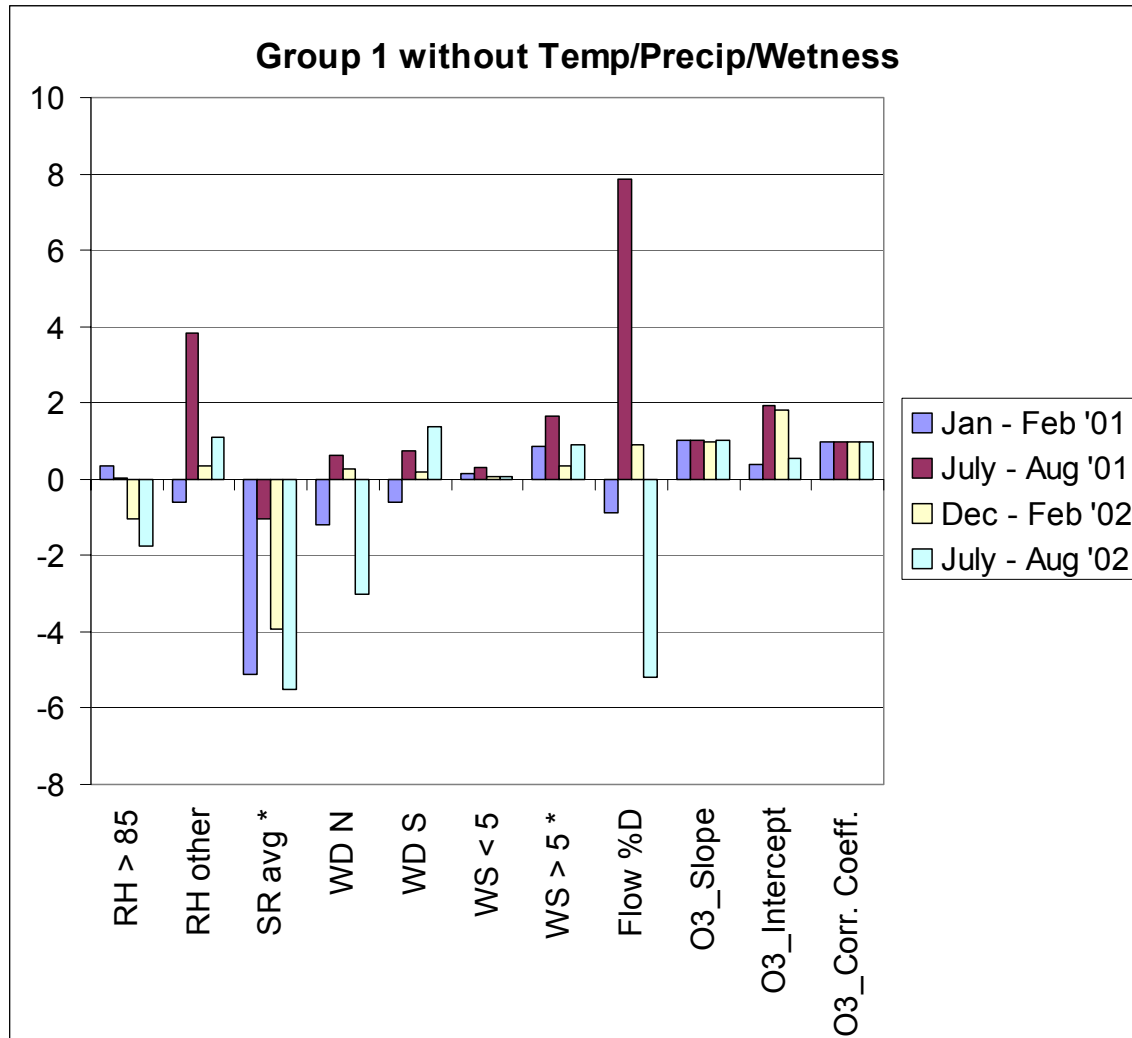
Figure 10. Locations of Group 1 and Group 4 Sites

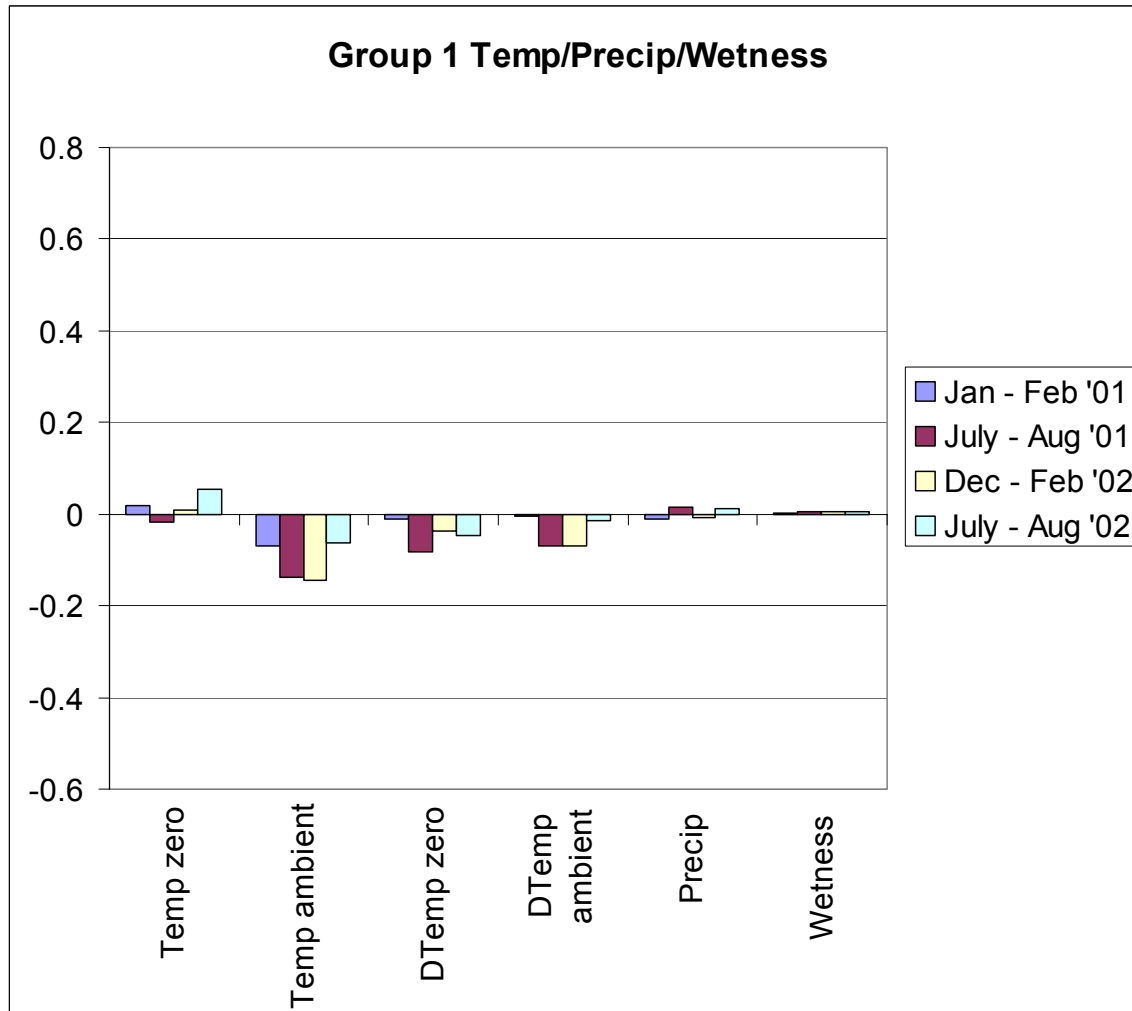
Figure 11a. Field Calibration Data for Group 1 Sites (2001-2002)



Note:

RH = relative humidity
 SR = solar radiation
 WD = wind direction
 WS = wind speed
 Coord. Coeff. = correlation coefficient

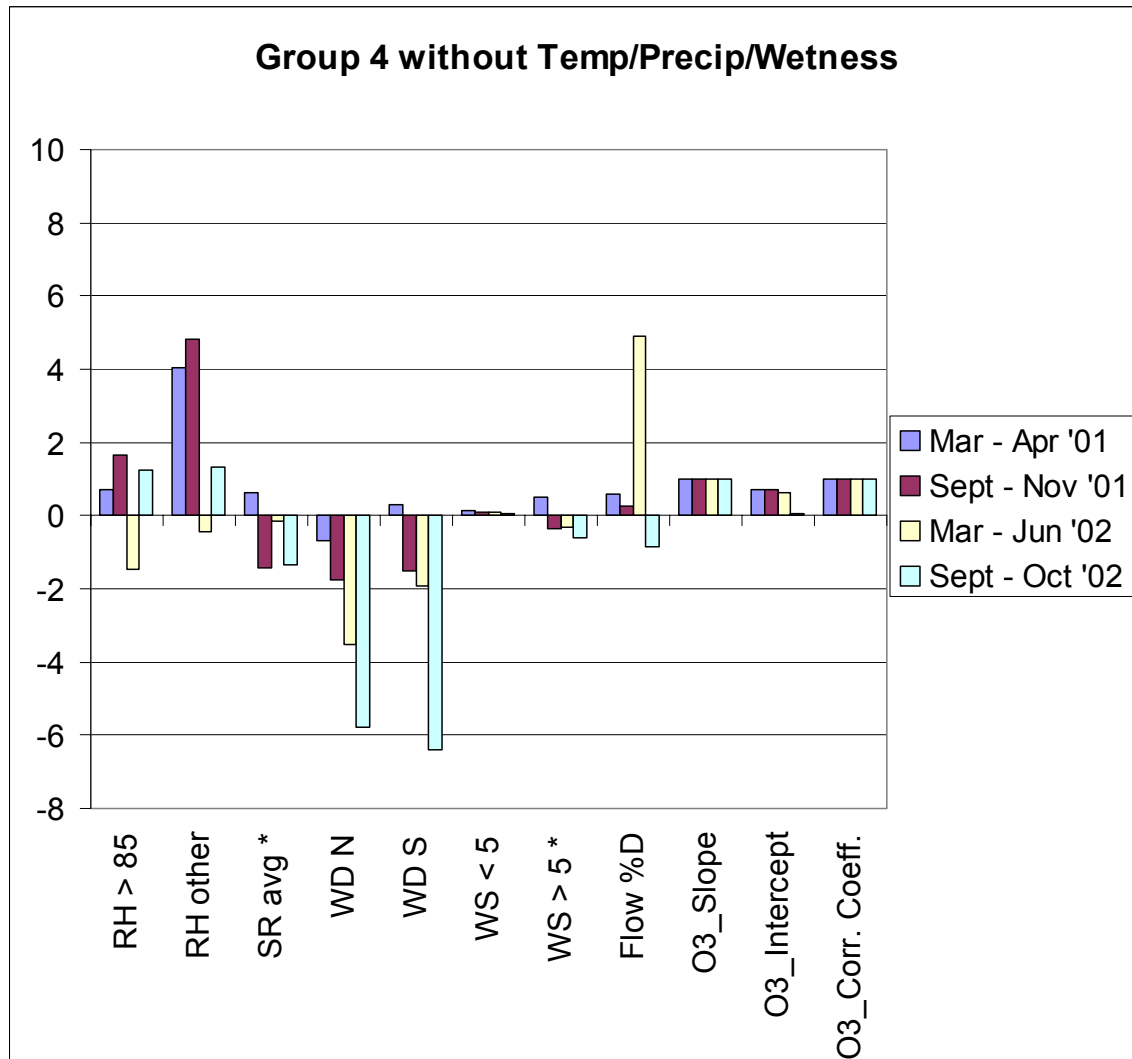
Figure 11b. Field Calibration Data for Group 1 Sites (2001-2002)



Note:

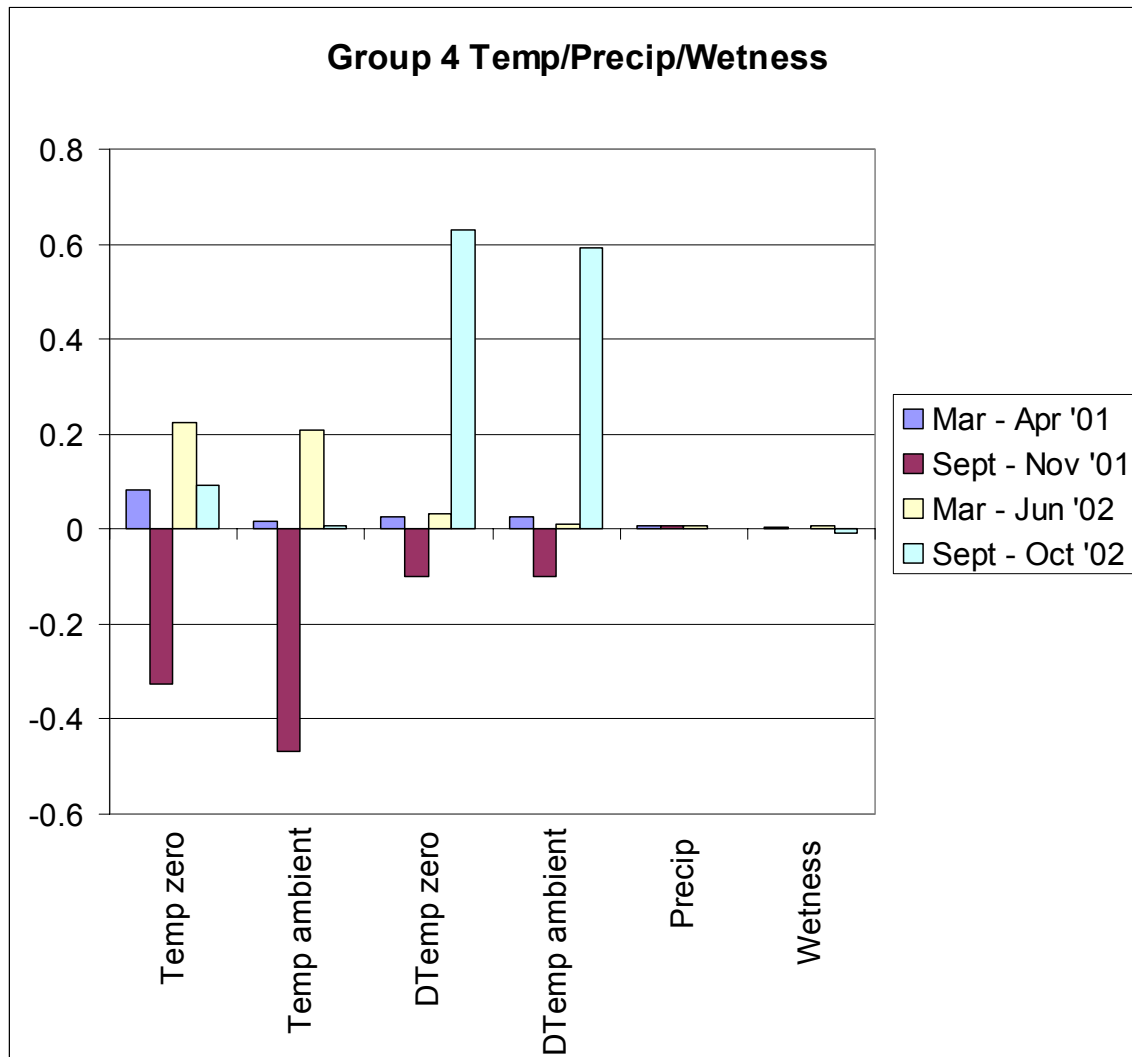
Temp = temperature
 DTemp = delta temperature
 Precip = precipitation

Figure 11c. Field Calibration Data for Group 4 Sites (2001-2002)



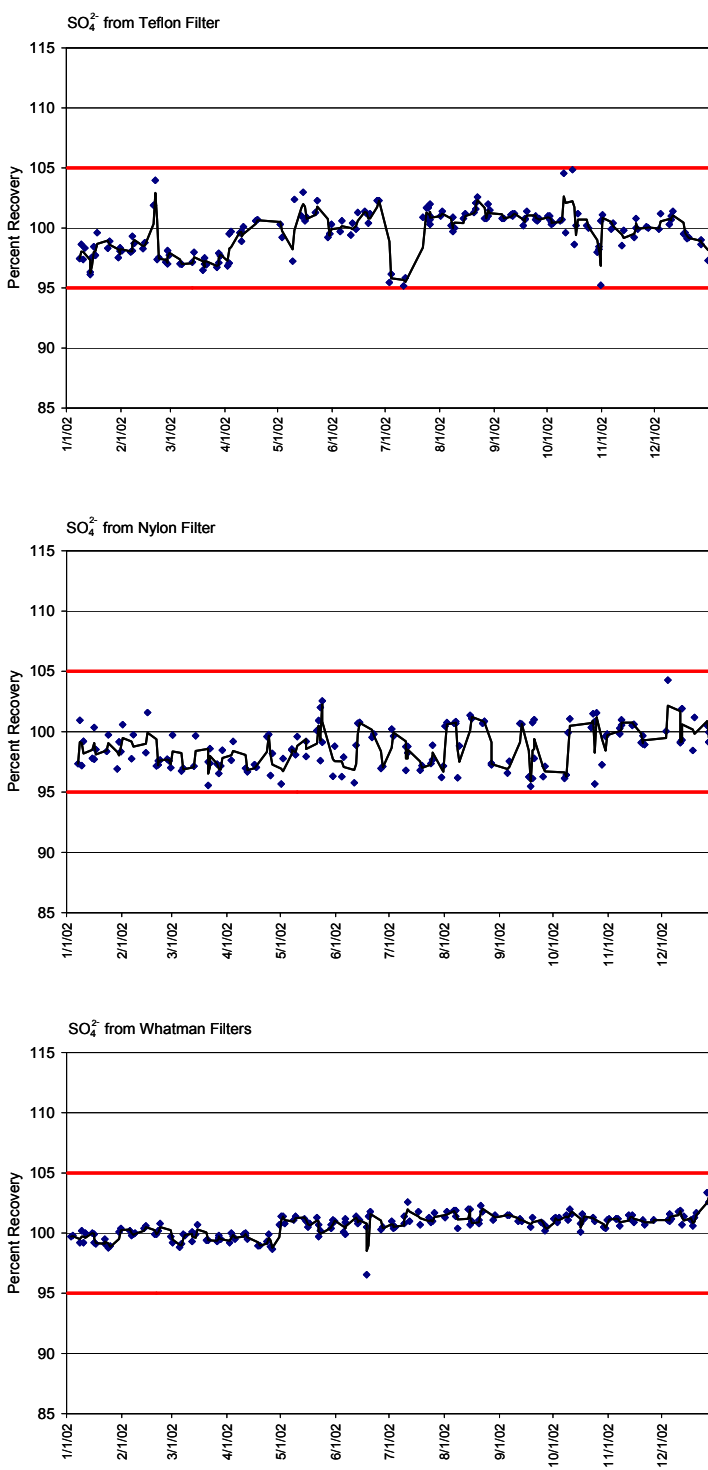
Note:

RH = relative humidity
 SR = solar radiation
 WD = wind direction
 WS = wind speed
 Coord. Coeff. = correlation coefficient

Figure 11d. Field Calibration Data for Group 4 Sites (2001-2002)**Note:**

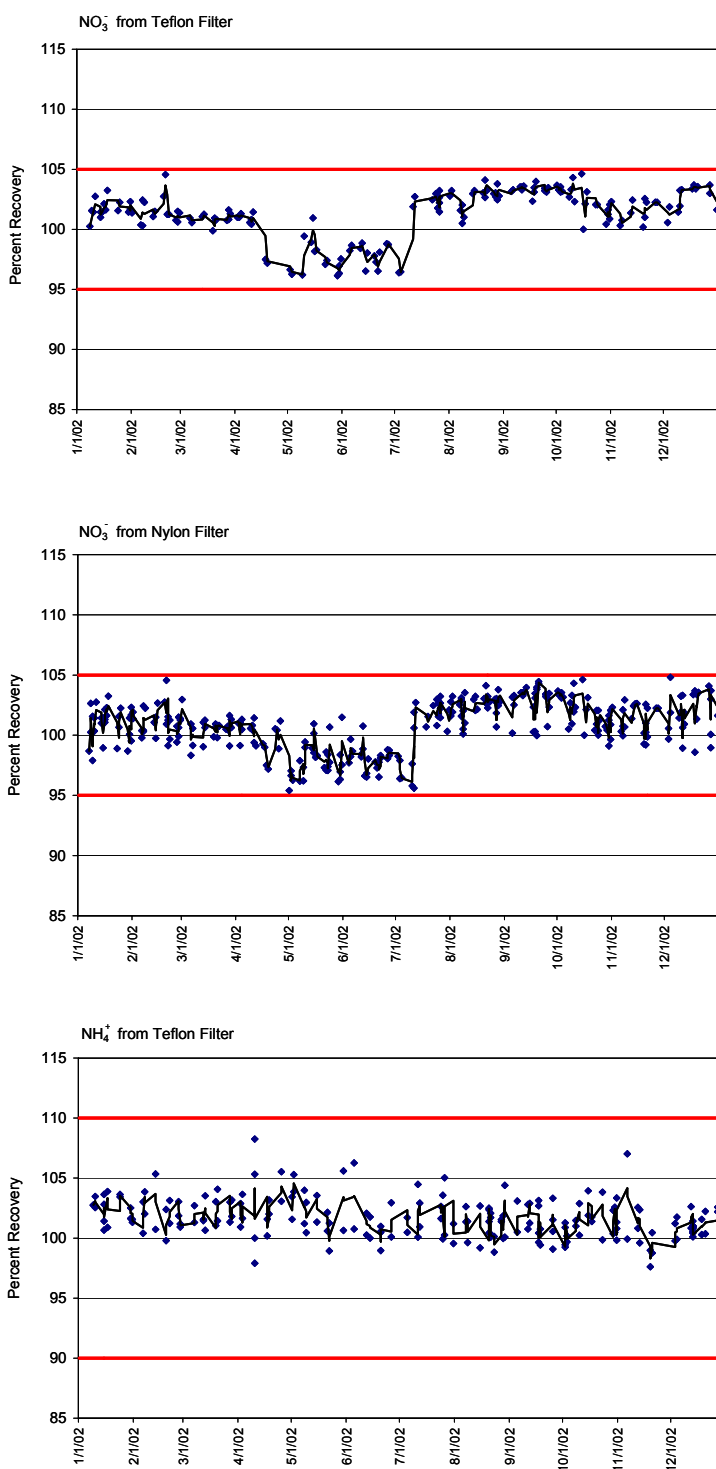
Temp = temperature
 DTemp = delta temperature
 Precip = precipitation

Figure 12. Laboratory Accuracy Data for 2002 (Percent Recovery of Reference Samples)
(Page 1 of 2)



Note:

The solid line was fit through the data points using a moving average with a period of two.

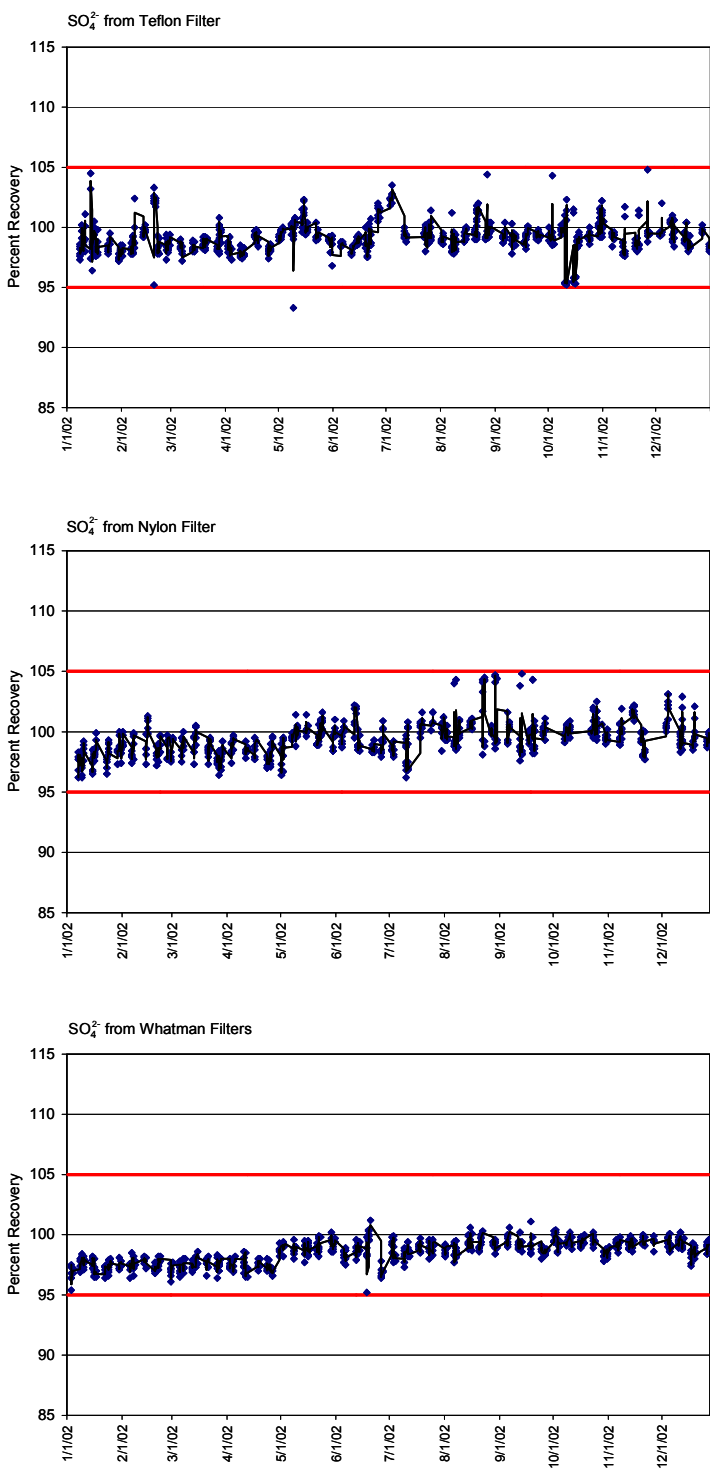
Figure 12. Laboratory Accuracy Data for 2002 (Percent Recovery of Reference Samples)

(Page 2 of 2)

Note:

The solid line was fit through the data points using a moving average with a period of two.

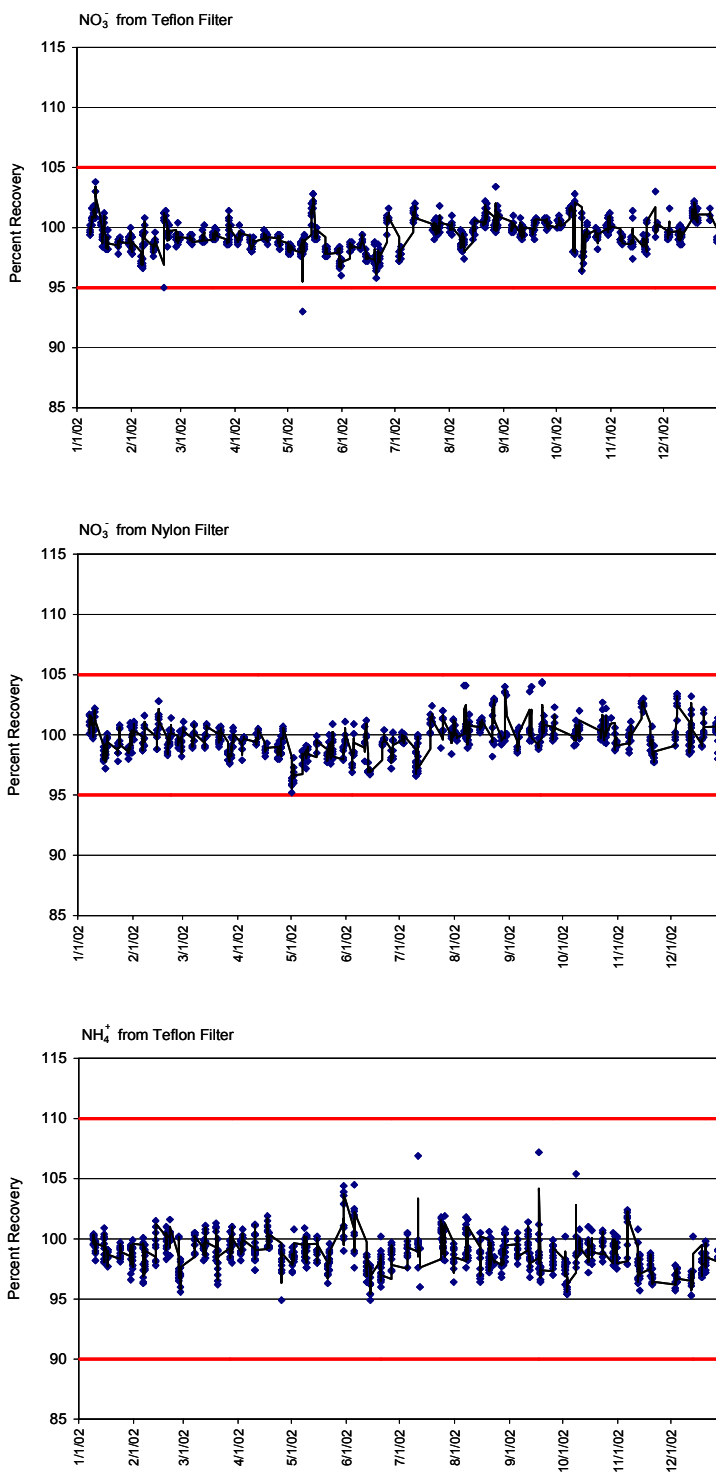
Figure 13. Laboratory Accuracy Data for 2002 (Percent Recovery of CVS)
(Page 1 of 2)



Note:

The solid line was fit through the data points using a moving average with a period of two.

Figure 13. Laboratory Accuracy Data for 2002 (Percent Recovery of CVS)
(Page 2 of 2)



Note:

The solid line was fit through the data points using a moving average with a period of two.

Comparability

Field Collocated Sampling Systems

In order to ensure the comparability of field data, siting and equipment specifications are consistent throughout the network. EPA or ASTM methods are used when available, SOP are identical at each site, and data are reported in conventional and standard units.

The precision of weekly modeled dry deposition (flux) rates were estimated for the collocated sampling stations at ROM206/ROM406, CO. The precision of the modeled flux rates are discussed in Chapter 6 of the CASTNet 2002 Annual Report (MACTEC, 2003a). The weekly flux estimates for SO_2 , HNO_3 , and SO_4^{2-} for the two monitoring stations are presented in Figures 6-5 through 6-7, respectively. The respective MARPD values are 11 percent, 8 percent, and 7 percent. These collocated sampling stations provide an excellent opportunity to evaluate inter-site comparability between EPA-sponsored sites and NPS-sponsored sites.

The collocated CASTNet/CAPMoN site at Egbert, Ontario, Canada also provides an excellent opportunity for comparison, especially since the field sampling methodologies are different: daily sampling for CAPMoN versus weekly (EGB181) and day/night (EGB281) sampling for CASTNet. Figure 14 presents the MARPD for 1995 through 2002 for EGB181/281. Day night averages were duration-weighted

and summed to facilitate comparison with the weekly samples. Results ranged from 3.4 percent to 9.3 percent for anions and ammonium and from 16.4 percent to 23 percent for metal cations. Figure 15 presents the MARPD resulting from comparison of daily CAPMoN and weekly CASTNet sampling. CAPMoN daily concentrations were simply averaged over the appropriate 7-day period for comparison with CASTNet samples. MARPD results ranged from 15 percent for particulate sulfate to 30 percent for gaseous nitric acid.

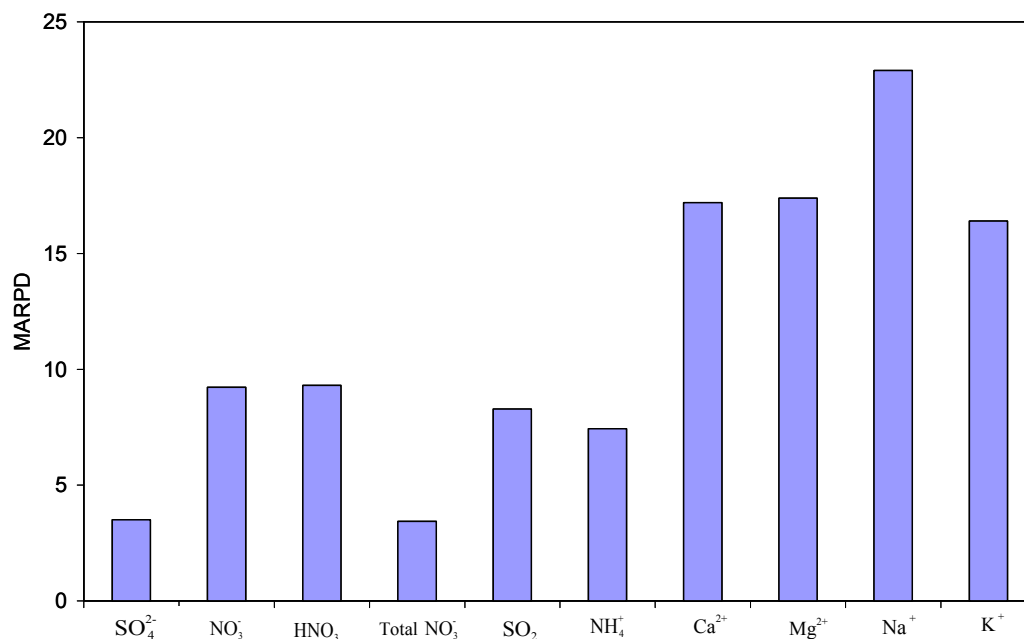
The Cooperative Institute for Research in the Atmosphere (CIIRA), located at Colorado State University, Fort Collins, CO, performed a comparison of particulate sulfate and nitrate concentrations reported by the Interagency Monitoring of Protected Visual Environments (IMPROVE) and CASTNet programs (Malm *et al.*, 2000). The data were found comparable for the particulate sulfate measurements. Particulate nitrate measurements showed widespread bias, likely due to differences in sampling protocol between the networks such as the use of denuders and cyclone particle separators by IMPROVE. CASTNet systems do not include either sampling device.

Laboratory Analysis

To ensure comparability of CASTNet laboratory results with results from other national monitoring programs, NIST-traceable standards are utilized and data are reported in standard units. The CASTNet laboratory participates regularly in laboratory intercomparison studies wherein blind samples are supplied to a group of participating laboratories for analysis. In these studies, results from the various laboratories are collected, statistics are generated, and results for each laboratory are reported. Figure 16 shows a summary of results for the U.S. Geological Survey

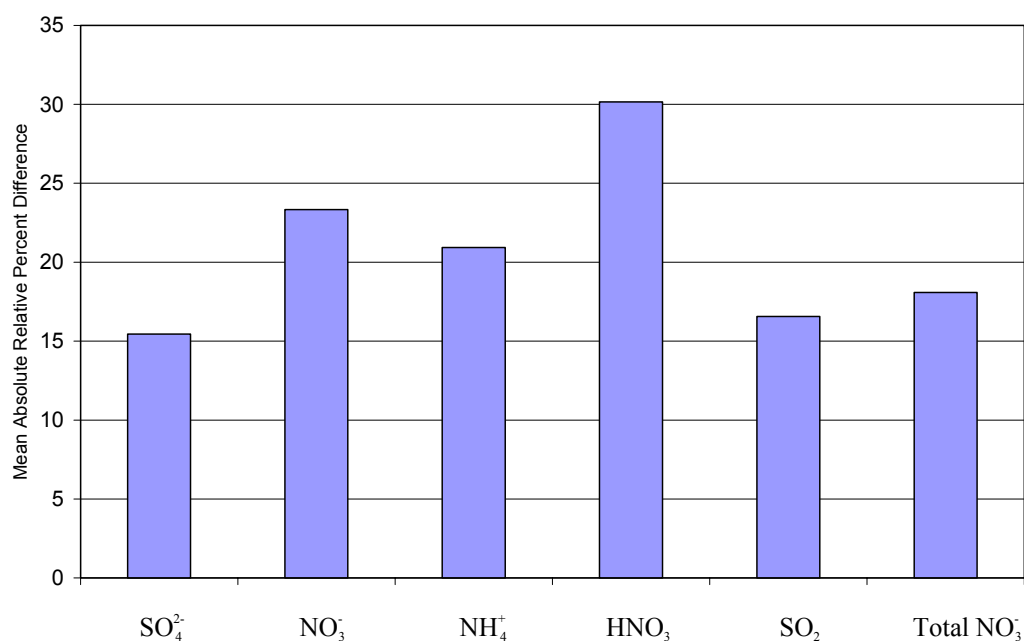
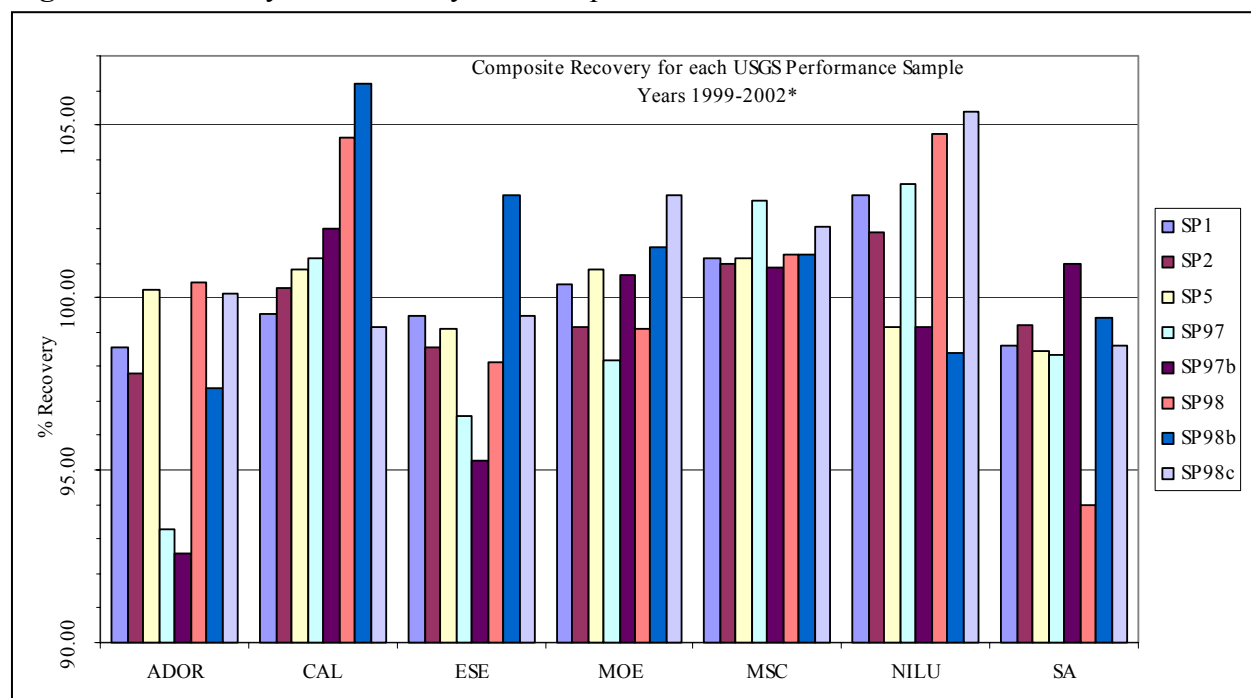
(USGS) Interlab program from 1999 through 2002. The average standard recovery results for the CASTNet laboratory (denoted “ESE”) were between 95 and 103 percent while the overall spread of the participating laboratories ranged from 93 to 106 percent. Figure 17 presents a 5-year median of study bias averages (percent biased parameters) for the Environment Canada (ECAN) National Water Research Institute (NWRI) National Laboratory for Environmental Testing (NLET) laboratory intercomparison program. The CASTNet laboratory 5-year median value was 6.6 percent.

Figure 14. Comparison of Concentration Data for EGB181/281, ON (1995-2002)

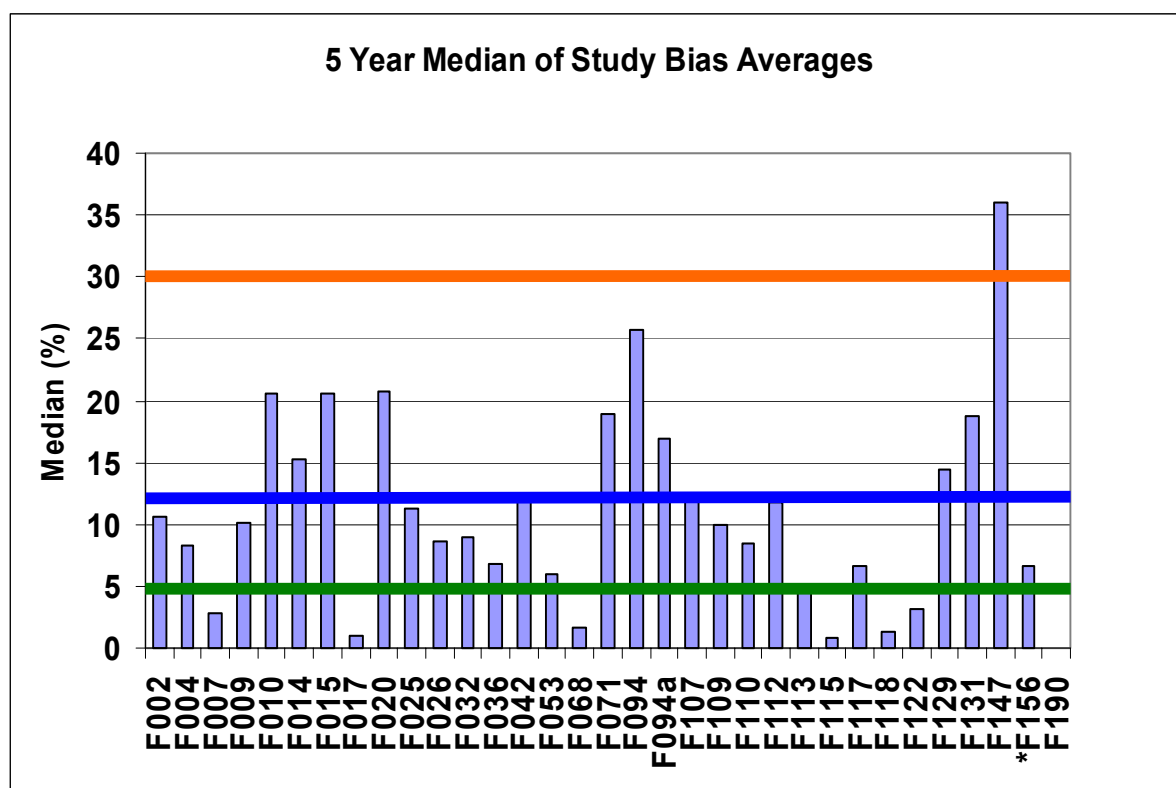


Note:

All metal cations are 2000-2002 only.

Figure 15. Comparison of CAPMoN and CASTNet Collocated Egbert, ON 1997 - 2001**Figure 16.** Summary of Laboratory Intercomparison Results for 1999 - 2002**Note:**

ADOR = Acid Deposition and Oxidant Research Center, Japan
 CAL = Central Analytical Lab
 ESE = MACTEC CASTNet Laboratory
 MOE = Ministry of Environment and Energy, Canada
 MSC = Meteorological Service of Canada
 NILU = Norwegian Institute for Air Research
 SA = Shepard Analytical
 SP1, etc. = blind reference sample numbers

Figure 17. Historical ECAN Study Results 1998 - 2002**Note:**

F02, F04, etc.	=	Laboratory ID Codes
*F156	=	MACTEC
Good	=	0 to 4.99%
Satisfactory	=	5 to 12.49%
Moderate	=	12.5 to 29.99%
Poor	=	>30%

Completeness

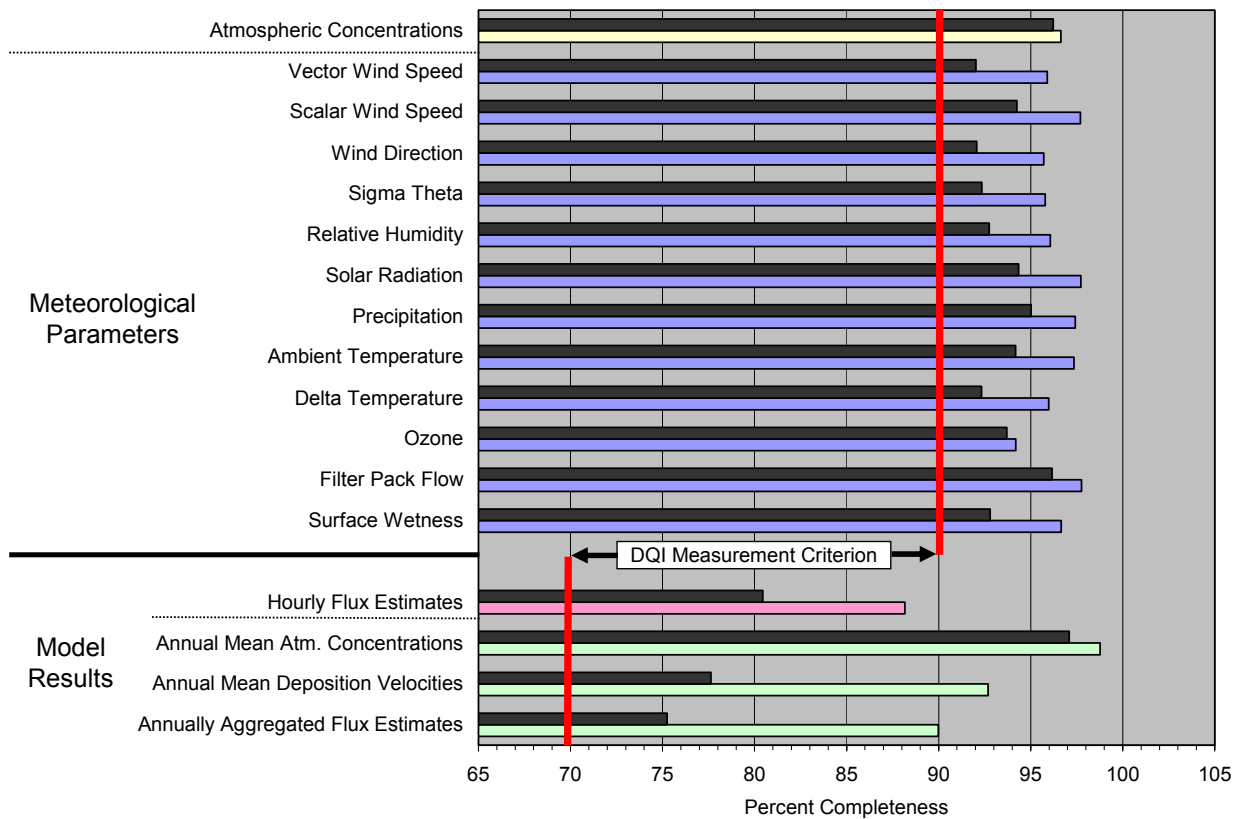
Completeness is defined as the percentage of valid data points relative to total possible data points. The CASTNet DQI criterion requires a minimum completeness of 90 percent for every measurement for each quarter. In addition, the data aggregation procedures discussed in Section D of the CASTNet QAPP (Harding ESE, 2001) require approximately 70 percent data completeness for hourly fluxes and weekly concentrations/fluxes in order to calculate weekly and quarterly values, respectively.

Figure 18 presents historical and 2002 completeness data for all sites for measured filter pack concentrations, continuous measurements, and for the calculated parameters: hourly dry deposition (flux) values, annual mean concentrations, annual mean deposition velocities, and annual flux estimates. The figure shows that historical and 2002 direct measurements met the 90 percent goal. Filter concentrations and flow values exceeded 95 percent completeness; ozone data completeness was approximately 94 percent. Hourly dry deposition fluxes were calculated from modeled V_d and

measured concentrations. As noted previously, the modeled V_d depend on several measured meteorological variables, i.e., one missing meteorological parameter or LAI value invalidates a V_d value. In other words, the completeness of the flux data depends on the combined completeness results for several parameters. The flux

completeness was greater than 75 percent, which meets the criterion for flux completeness. The completeness of the annual mean concentrations, deposition velocities, and flux estimates all met their associated criteria.

Figure 18. Historical Percent Completeness of Measurements and Modeled Estimates



Note:
 Black = Historical data (1990-2001)
 Colors = 2002 data